Reconstruction of occupational mercury exposures at a chloralkali plant

P L Williams, H Frumkin, M L Pierce, C C Manning, L Elon, A G Sanders

Abstract
Objective—To reconstruct historical workplace exposure to mercury (Hg) from 1956 to 1994 at a large chloralkali factory for use in a current epidemiology study of the factory.

Methods—All job activities of the employees were classified into one of 16 exposure categories, and the dates of changes in the processes were identified. Exposures to Hg for each job category, at each period of the plant’s operation, were then reconstructed from several data sources. A job-time period-exposure matrix was created, and the individual exposures of former workers were calculated. Data on exposure to Hg in air were compared with modelled concentrations of Hg in air and data on urinary Hg of the employees.

Results—Within an exposure category, concentrations of Hg in air were fairly constant for the first 20 years of the factory’s operation, but began to increase in the late 1970s. Employees working in the cell room had the greatest exposures to Hg. The exposure estimates had significant correlations (p<0.001) with the urinary data and were well within the modelled range of concentrations of Hg in air.

Conclusions—The highest exposures occurred from 1987 until the plant closed in early 1994 with some exposure categories having time weighted average exposures to Hg greater than 140 µg/m³.

Keywords: mercury; chloralkali; occupational exposure; job exposure matrix

This paper describes the historical reconstruction of exposure to Hg among employees at a chloralkali plant that operated from 1956 to 1994 in Brunswick, Georgia, USA. Although caustic soda and chlorine production using the chloralkali process has a long history, few studies have measured occupational exposures to Hg. This study involved the development of a job-exposure matrix based on historical workplace measurements. The exposure estimates from the matrix were validated with two independent strategies: estimating concentrations of Hg in air by modelling rates of change of room air and known Hg losses within the factory; and comparing data on urinary Hg concentrations of the employees with predicted concentrations of Hg in air. Also, the exposure estimates from the matrix were compared with exposure estimates from previous studies of chloralkali plants. Finally, the reconstructed data on exposure to Hg were used in a historical cohort study of the workforce, the results of which are reported separately.

From 1956 to the end of 1994, a large chloralkali production factory operated in Brunswick, Georgia, USA. The plant was situated on a 550 acre marshy site adjacent to the mouth of the Turtle River as it empties into the Atlantic Ocean. The factory used electrolytic cells based on Hg (Solvay process) located in two large cell rooms to convert sodium chloride and water into chlorine, caustic soda (or soda ash), hydrochloric acid, and hydrogen gas. This operation resulted in considerable releases of Hg into the workplace and the ambient environment leading the Georgia Environmental Protection Division to close several adjacent waterways to fishing in the early 1990s. In February 1994, the Georgia Environmental Protection Division revoked the factory’s National Pollutant Discharge Elimination System and air quality permits, and the plant ended operations. The site was subsequently designated a Superfund hazardous waste site by the United States Environmental Protection Agency, and extensive remediation efforts were completed during the late 1990s.

Concerns about the health of employees related to exposure to Hg began to surface in the middle to late 1980s and several investigations were performed to assess exposures of employees. It was later learned that over 227 000 kg Hg used at the site were unaccounted for and may have been lost to the environment. In response to local concerns, an epidemiological study of the former employees was initiated in 1997, with funding from the United States National Institute for Environmental Health Sciences.

Materials and methods
SAMPLING DATA ON Hg IN AIR
Sampling data on Hg in air were collected at the plant from several sources. Factory personnel routinely collected Hg vapour readings and recorded the air concentrations on a standard form that provided a sketch of the area with the sample, location, and date. This sampling was performed throughout both floors of the two cell rooms and occasionally in other areas including the lunch room, locker room, laundry area, Hg still area, and products area. These were area samples, not personal samples, collected with a hand held Bacharach Mercury Sniffer. Air sampling forms were found for 488 separate days of exposure between 1967 and 1993, representing about 25 000 separate readings of concentrations of Hg in air.
Table 1  Chloralkali facility job titles grouped into similar categories of exposure to Hg

<table>
<thead>
<tr>
<th>Exposure group</th>
<th>Job titles included</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury handler</td>
<td>Mercury handler</td>
</tr>
<tr>
<td>Cell repair</td>
<td>Cell repair, cell assembly</td>
</tr>
<tr>
<td>Cell room</td>
<td>Assistant cell operator, assistant foreman, cell operator</td>
</tr>
<tr>
<td>Cell room; others</td>
<td>Shift foreman, tester, engineer, production specialist</td>
</tr>
<tr>
<td>Products area</td>
<td>Acid loader, bleach operator, products operator, assistant products operator</td>
</tr>
<tr>
<td>Brine area</td>
<td>Salt plant operator, brine processor or assistant, saturation operator</td>
</tr>
<tr>
<td>Welding area</td>
<td>Cell welder</td>
</tr>
<tr>
<td>Machinist</td>
<td>Machinist</td>
</tr>
<tr>
<td>Mechanics or maintenance</td>
<td>Electrician, maintenance painter, maintenance foreman, instrument technician, laundry room attendant</td>
</tr>
<tr>
<td>Relief operators</td>
<td>Relief operator, adjuster, utility operator</td>
</tr>
<tr>
<td>Broiler room</td>
<td>Broiler room operator</td>
</tr>
<tr>
<td>Management</td>
<td>Plant manager, operations manager</td>
</tr>
<tr>
<td>General labourer</td>
<td>Storeroom attendant, laboratory technician, tank car painter, tank car service</td>
</tr>
<tr>
<td>Plant office</td>
<td>Maintenance clerk, shipping foreman, production supervisor, technician supervisor, security, maintenance planners, production manager, production superintendent</td>
</tr>
<tr>
<td>Main office</td>
<td>Employee relations manager, plant controller, senior clerk, payroll clerk, accounting clerk, purchasing agent, receptionist, switchboard operator, purchasing clerk, senior laborer, dock operator</td>
</tr>
<tr>
<td>Environmental operator</td>
<td>Environmental operator, wastewater treatment operator</td>
</tr>
</tbody>
</table>

Two federal agencies, the National Institute for Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA), performed Hg air sampling within several areas of the factory. A NIOSH health hazard evaluation was performed in late 1987 to the end of April 1988, and OSHA inspections were conducted in 1988, 1990, and 1992. Finally, scientists from Duke University performed a personal air sampling study at the site in 1988. These three sources (NIOSH, OSHA, and Duke) yielded a total of 48 personal samples of Hg in air over 15 days.

EMPLOYEE INTERVIEWS
Ten former employees of the factory who had experience in all aspects of plant operations from 1956 to 1994 were extensively interviewed. They represented management, supervision, and union positions. All but one of the people had worked at the site for over 20 years and collectively they had about 250 years of experience at the factory. The individual interviews ranged in duration from 1 hour to several days and assisted in interpreting the factory records previously described. The interviewees provided details on historical changes within the factory and the work practices (use of personal protective equipment, time spent in job duties, activities performed, etc) for each job title.

RECONSTRUCTION OF EXPOSURE
From the interviews and a review of personal records, 55 job titles were identified. Based on a comparison of potential exposures to Hg from specific work activities, these job titles were grouped into 16 exposure groups (table 1). Extensive estimates were made for the amount of time people in each exposure group spent in specific areas of the factory. This location specific information on duration of exposure was used to derive time weighted average (TWA) formulas for exposure to Hg for specific exposure groups that allowed the area readings for Hg to be used to estimate individual exposures.

For each exposure group the TWA formulas were used for each day that sampling data existed and then all the values for a year were averaged to derive an estimated concentration of Hg in air for a specific year. For the years before the collection of any sampling data of Hg in air (1956–66), the mean concentration of Hg in air from 1967–74 was used, based on employee reports that the production process and work practices had not changed appreciably from the 1950s to the early 1970s. For other years for which no readings of Hg in air were available (1975–7, 1981–6, and 1989), we interpolated from the earlier and later years based on employee accounts of factory conditions (maintenance, production levels, operating conditions, controls in place) during those years.

We created a matrix that provided the estimates of exposure to Hg for each exposure group (table 1) for each year from 1956 to the end of February 1994. Personnel records that provided the dates for each job title that the person held were obtained for all former workers. For each former worker participating in the epidemiology study, we combined these two data sources by creating an individual matrix that accounted for each job held from the first to the last, with the associated exposure level for each. For each person, we could then calculate the cumulative exposure, the mean exposure, and the peak exposure, with a computer program written for this purpose. These metrics were used in the epidemiological study.

DATA VALIDATION
We assessed the estimates of exposure to Hg generated by this process in two ways. Firstly, we compared them with predicted concentrations of Hg in air in the cell rooms that we calculated based on rates of change and losses of Hg in air. Secondly, we compared them with personal data on urinary Hg.

The dimensions and equipment space of the two cell rooms were known, permitting calculation of the air volume of each floor. From employee interviews, we collected information on the ventilation design specifications of the building and the conditions of operation. The factory’s Environmental Protection Division air permit allowed the release of 2.27 kg Hg/day. The factory’s engineering staff,
through a mass balance approach, had calculated that about 1.13 kg Hg were lost to the ambient environment through the boiler, and that the rest (about 1.14 kg Hg) was released into each cell room (0.57 kg Hg/cell room). It was assumed that these Hg losses were uniform over a 24 hour day throughout each cell room. From the room volume and the exhaust capacity of the fans operating within each cell room, the total volume of air exchanged within each room could be calculated. The ranges of concentrations of Hg were modelled for different seasons of the year based on typical exhaust fan operations and compared with those predicted from the TWA formulas.

As well as data from sampling Hg in air, in the early 1970s the plant began collecting urinary Hg samples from employees, on about a quarterly basis. Although urinary samples were collected and analyzed, correction for dilution of urine with either creatinine or specific gravity was not performed until 1988. As uncorrected values can lead to extensive misclassification, the uncorrected urinary data were not used in this study. Also, the handwritten records of urinary Hg values for some of the time intervals were sloppy and lacked any reference to quality control procedures or standardisation. Such data were also judged unusable. However, there were 590 urinary Hg values from November 1988 to the end of May 1991 that were corrected for specific gravity and seemed to have been rigorously measured and recorded. These data came from 78 workers representing 13 of the 16 exposure groups in table 1. For each of the 78 workers, we identified the start and end date of the available urinary readings, and averaged these readings. We then calculated the mean, cumulative, and peak exposures for the period beginning 60 days before the first urinary Hg reading and ending 60 days before the final urinary Hg reading, to account for the published half life of urinary Hg of 40–60 days. We compared the urinary values with each of the reconstructed exposures to Hg concentrations with Spearman correlation coefficients.

**Correlation for interference by chlorine gas**

At least one previous study found that chlorine gas interfered with UV detection instruments that made direct readings of Hg. Chlorine gas can chemically interact with the elemental Hg vapour to form mercuric chloride, which is not detected by the UV method, causing negative interference. This negative effect has been found to be directly proportional to the amount of chlorine gas present.

Chlorine gas was continually present at the factory in our study, requiring occasional plant shutdowns due to chlorine releases and routine use of respiratory protection against chlorine. The precise concentrations of chlorine that were present are not known. The NIOSH investigators performed some limited sampling of chlorine in air and found the air concentrations to be generally below 1.5 μg/m³ (six of seven samples). Workers were questioned about the presence of chlorine during our interview process and reported that personnel recording the Hg readings avoided areas where chlorine concentrations were noticeably irritating. The air concentration of chlorine gas that usually causes irritation is reported to be above 1.5 μg/m³. Accordingly, we assumed, based on the interviews and NIOSH findings, that the chlorine gas concentration was at or below this value when Hg readings were collected.

If interference by chlorine affected our Hg data, it would only have affected the area samples collected with the Bacharach Mercury Sniffer; the personal samples that were actively collected on sorbent tubes and later analyzed by atomic absorption would have been unaffected. To assess whether the direct reading sampling data were affected by the presence of chlorine, we sought to compare results from concurrent sampling methods. From the data recovered at the site, active personal samples were collected concurrently with area samples on only 8 separate days (table 2). We used the data from these days to perform a limited comparison between the personal active sampling data and the predicted TWA concentrations with the rank order correlation coefficient, a comparison of the relative order from low to high.

**Results**

**Exposure estimates**

To measure exposure trends over time, the readings of Hg in air (about 25 000) from throughout the site collected by factory personnel from 1967 to 1993 were sorted by year and annual means were calculated. These values ranged from about 5 to slightly above 100 μg Hg/m³ of air. The concentrations increased over the years with the highest concentrations in air coming in the late 1980s and early 1990s. This finding confirmed the impressions of employees interviewed who thought that conditions at the site began to worsen in the early 1980s and declined until the plant closed in 1994.

The next step was to apply the TWA formulas to exposure groups and calculate annual estimates of exposure to Hg. Figure 1 provides the annual estimates of exposure to Hg for cell room jobs (including Hg handler, cell repair/assembly, and other cell room workers), the products areas exposure group, and a mean of the remaining 11 exposure groups grouped as “average of all other workers”. Within each of these categories, the Hg concentrations began to increase in the late 1970s and remained high.

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Table 2  Comparison of concurrent direct reading and active air sampling data for the same exposure category

<table>
<thead>
<tr>
<th>Date (separate days)</th>
<th>Predicted TWA from direct reading instrument (µg Hg/m³ air)</th>
<th>Active personal sampler (µg Hg/m³ air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 1988</td>
<td>9</td>
<td>44</td>
</tr>
<tr>
<td>April 1988</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>April 1988</td>
<td>33</td>
<td>45</td>
</tr>
<tr>
<td>April 1988</td>
<td>45</td>
<td>57</td>
</tr>
<tr>
<td>April 1988</td>
<td>53</td>
<td>223</td>
</tr>
<tr>
<td>September 1988</td>
<td>61</td>
<td>165</td>
</tr>
<tr>
<td>September 1988</td>
<td>97</td>
<td>140</td>
</tr>
<tr>
<td>September 1988</td>
<td>97</td>
<td>234</td>
</tr>
</tbody>
</table>
until the factory closed in 1994. On average, the cell room personnel had the highest exposures to Hg of anyone in the factory, as expected based on employee interviews. Within the cell room, the Hg handlers and cell repair/assembly categories had the highest exposure to Hg concentrations (fig 2).

**DATA VALIDATION**

Each cell room contained 28 fans capable of each moving 908 m³ air/minute. The primary function of these fans was to cool the cell rooms, which reached temperatures of over 37°C. With the heat produced by the process and the warm climate of Brunswick, Georgia, most of the fans were operated during most of the year. At times when the outside temperatures were unusually low, some of the fans would be turned off, but even then it was reported that at least two fans would always be running. Based on a range of two to 28 fans in operation, moving an estimated 2.6×10⁶ to 3.7×10⁶ m³ air through the room daily, the rough volume of 23,391 m³ for the building, and an expected daily loss of 0.57 kg Hg in each cell room, the predicted concentration of Hg in air in the cell rooms would range from about 15–220 µg Hg/m³ air with the lower end of the range representing more dilution from outside air (operation of all 28 fans) and the higher end representing less dilution (only two fans operating). The actual exposures of employees would be affected by many things—such as the amount of time spent in the cell room, the air mixing conditions in the room, the work activities, the actual amount of Hg released, and the operating condition of the fans. None the less, the calculated range corresponds well to the TWAs estimated for cell room employees (fig 2).

There were 78 former workers for whom data on urinary Hg during 1988–91 were available, and for whom we reconstructed job histories and associated exposures. These 78 workers had mean urinary Hg concentrations of 72.4 µg/l, with a range of 13.0–191.5 µg/l (corrected to a specific gravity of 1.024). The Spearman correlation coefficients were 0.52 for the mean exposure, 0.69 for the cumulative exposure, and 0.74 for the maximum exposure, all with p<0.0001. One previous study¹² reported that data on urinary Hg are the best predictors of exposure to Hg and these values indicate that our exposure estimates are reasonable predictors of exposure to Hg.

**CORRECTION FOR INTERFERENCE BY CHLORINE GAS**

As shown in table 2, the active, personal samples always yielded a higher Hg concentration than the predicted TWA from the concurrent direct reading area sample but they have a similar trend (higher active samples correspond to higher predicted TWA Hg concentrations). The rank order correlation coefficient for the data is 0.85 (p<0.01) and the Pearson’s correlation coefficient is 0.60. Based on these findings it was assessed that the estimated exposure of an employee to Hg to be used in the concurrent epidemiology study should be increased to account for the potential interference by chlorine gas. Smith et al found that concentrations of chlorine in air in the 1.5 mg/m³ range (concentration of chlorine in air associated with irritation) resulted in about a 20% reduction in the concentrations of Hg in air recorded by the instruments that read Hg concentrations directly. As this concentration of chlorine in air is thought to be the upper range of exposure to chlorine in the area where Hg readings were taken, the estimates of exposure to Hg were increased by 20%.

This alteration results in the cell room Hg concentration increasing to a range of 18–147 µg/m³. These increased values were used in the concurrent epidemiology study¹ and individual exposure estimates for mean, cumulative, and peak concentrations were derived. These exposures were consistent with values reported from other chloralkali factories¹²–¹⁴ and well within the range predicted from rates of change of Hg in air, and do not affect the correlation with urinary data of the employees.

**Discussion**

Only one recent study¹² reports exposures to Hg in a chloralkali factory and several older studies also were identified.¹⁰–¹⁴ With the older studies, area sampling data of air were

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**Figure 1** Annual mean estimates of exposure to Hg for peripheral areas of the factory.

**Figure 2** Annual mean estimates of exposure to Hg for employees within the cell room.
Reconstruction of occupational mercury exposures at a chloralkali plant

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North American factories in the middle to late States plants (1957–62); a range of 1–270 µg/m³ in two German plants personal air samples (very similar to our data). Mercury Sniffs were primarily collected with instruments that took direct readings—such as the Bacharach Mercury Sniffers—supplemented with some limited personal air samples (very similar to our data). The most recent study was performed for an exposure period 1990–7 and used personal sampling data. The cell room TWA concentrations of Hg in air for the older studies were reported to be 80–110 µg/m³ for two United States plants (1957–62); a range of 1–270 µg/m³ with 60% at or below 50 µg/m³ for 21 operations in the United States and Canada in the late 1960s; generally between 50 and 100 µg/m³ for the high exposure groups from two North American factories in the middle to late 1970s and usually between 30 and 90 µg/m³ with a mean of 75 µg/m³ in two German plants (1976–7). The recent study reported that the cell room maintenance workers had the highest exposures to Hg but provided only an overall mean (SD) factory exposure level for all employees of 22 (35) µg/m³. The years covered in the older studies—early 1960s to early 1980s—should represent similar working conditions present within the chloralkali industry. In our study, during these same years a range of about 15–40 µg/m³ TWA Hg concentrations (or about 20–50 µg/m³ when corrected for chloramine) was estimated for cell room employees, which is at the low end of the range reported in other studies.

Our study found a much higher exposure to Hg in the later years of the factory’s operation (late 1970s to closure in 1994) compared with the earlier years of operation. One might conclude from the data that the exposure estimates represent two separate data sets that may have resulted due to differences in monitoring Hg or from increased interest from outside agencies causing improved monitoring methods at the site. We do not think that this was the case. The workforce at the site was stable and the Hg monitoring was performed by basically the same group of workers with the same instrument and methods. Also, exposure to Hg started to increase in the late 1970s and steadily rose with the highest exposures in 1987, before the inquires by governmental agencies. In fact, it seems that the concentrations improved for several years (1988–91) after outside interest from governmental agencies. For these reasons, we think that the estimates represent actual exposures to Hg over the course of the factory’s operation.

This paper shows the systematic historical reconstruction of past exposures for use in an epidemiological study. As in many such efforts, we had to rely on several types of data, including air sampling, measurements of urinary Hg, and recollections of former workers. Much of the primary data had not been published, existed in the form of handwritten records in dusty boxes, and was of unclear quality. Hence, an important initial challenge was to assess the quality of the data. We initially planned to use all available data on urinary Hg, but on inspection, we were not confident in the quality of most of these data. Such judgments are an important aspect of reconstruction of historical exposure.

It is important to note that our exposure estimates are based on concentrations in air. However, actual exposures could have been higher due to dermal absorption. Biomarkers of exposure, when available, integrate different routes of exposure, offering an important advantage over workplace sampling of a specific medium.

Two aspects of this process are noteworthy. Firstly, we attempt to validate our reconstructed exposures in two ways: through modelling concentrations of Hg in air, and through comparison with concentrations of urinary Hg. Both approaches were straightforward and feasible with the available data (albeit a truncated urinary Hg data set), and both confirmed the results of our reconstruction. We recommend such efforts as validation in historical assessment of exposure. Symanski et al. compared data on exposures of Hg in air, blood Hg, and urinary Hg, and found that creatinine corrected urinary Hg better discriminated worker’s exposures than the other two. In our study data on urinary Hg were too limited to use (except as described above) and concentrations of Hg in air had to be used as the principal exposure estimate.

Secondly, we considered the issue of interference with direct readings of Hg by chlorine. This phenomenon, although well established, has not been considered in previous studies. Although it did not result in major changes in our exposure estimates, such corrections could be important in calculating dose-response relations.

Electromagnetic fields associated with the Solvay process may also interfere with direct reading measurements of Hg, but this interaction is less clear, and the effect may be positive or negative. The NIOSH investigators did perform measurements of electromagnetic fields at the site and found levels ranging from 0–0.05 T with most being less than 0.01 T; all of which are within acceptable occupational exposure levels. The interviews of the employees showed that the Bacharach Mercury Sniffers were always zeroed and checked for calibration outside the cell rooms, which should have limited any interference from electromagnetic fields.

In conclusion, this paper provides a detailed description of a historical reconstruction of occupational exposure to Hg in a chloralkali plant over nearly 40 years of exposure, with area readings from an instrument that reads Hg directly, supplemented by limited data on personal sampling and urinary Hg. The Hg concentrations were found to be highest in the cell room where some job categories had peak air concentrations above 145 µg/m³. The estimates of exposure in air correlate with data on urinary Hg of the employees and are well within the range of Hg data predicted from rates of change of Hg in air and from other studies from similar processes.

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